

AD-A212 927

(4)

DTIC File Copy

OFFICE OF NAVAL RESEARCH

Contract N00014-86-K-0043

TECHNICAL REPORT No. 111

Optical Nutation in Polymers Irradiated by Ultrashort Laser Pulses

by

Xiao-shen Li, D. L. Lin, Thomas F. George and Xin Sun

Prepared for Publication

in

Physical Review B

Departments of Chemistry and Physics
State University of New York at Buffalo
Buffalo, New York 14260

September 1989

Reproduction in whole or in part is permitted for any purpose of the
United States Government.

This document has been approved for public release and sale;
its distribution is unlimited.

DTIC
ELECTED
SEP 26 1989
S E D
(2)

89 9 25 042

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

Form Approved
OMB No. 0704-0188

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified		'b RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE			
4. PERFORMING ORGANIZATION REPORT NUMBER(S) UBUFFALO/DC/89/TR-111		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
6a. NAME OF PERFORMING ORGANIZATION Depts. Chemistry & Physics State University of New York	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION	
6c. ADDRESS (City, State, and ZIP Code) Fronczak Hall, Amherst Campus Buffalo, New York 14260		7b. ADDRESS (City, State, and ZIP Code) Chemistry Program 800 N. Quincy Street Arlington, Virginia 22217	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER Contract N00014-86-K-0043	
8c. ADDRESS (City, State, and ZIP Code) Chemistry Program 800 N. Quincy Street Arlington, Virginia 22217		10. SOURCE OF FUNDING NUMBERS	
11. TITLE (Include Security Classification) Optical Nutation in Polymers Irradiated by Ultrashort Laser Pulses	PROGRAM ELEMENT NO. PROJECT NO. TASK NO. WORK UNIT ACCESSION NO.		
12. PERSONAL AUTHOR(S) Xiao-shen Li, D. L. Lin, Thomas F. George and Xin Sun			
13a. TYPE OF REPORT	13b. TIME COVERED FROM _____ TO _____	14. DATE OF REPORT (Year, Month, Day) September 1989	15. PAGE COUNT 20
16. SUPPLEMENTARY NOTATION Prepared for publication in Physical Review B			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) POLYMERS OPTICAL NUTATION IRRADIATION PHONON EFFECTS SHORT LASER PULSES EXCITONS	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) The transient behavior of the optical susceptibility of polydiacetylene induced by an ultrafast pump field is investigated. Within a two-level model which includes phonon effects phenomenologically, an analytical expression for the nonlinear susceptibility is obtained. In addition to spectral hole burning, the novel phenomenon of optical nutation is found. Both this nutation and the shape of the hole depend sensitively on the detuning between the exciton frequency and the sum of the pump field and the phonon mode frequencies. The electronic state and phonon-mediated optical Stark blue shift are also found in this model. The results are in qualitative agreement with experiments and indicate that the steady-state approximation is reliable only when the pulse of the pump field is longer than several exciton lifetimes.			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. David L. Nelson		22b. TELEPHONE (Include Area Code) (202) 696-4410	22c. OFFICE SYMBOL

Optical nutation in polymers irradiated by ultrashort laser pulses



Xiao-shen Li*, D. L. Lin and Thomas F. George
Department of Physics and Astronomy
State University of New York at Buffalo
Buffalo, New York 14260

and

Xin Sun
Center of Theoretical Physics
Chinese Center of Advanced Science and Technology (World Laboratory)
P. O. Box 8730
Beijing 100080, People's Republic of China

and

Department of Physics
Fudan University
Shanghai 200433, People's Republic of China

Abstract

on For	
RA&I	<input checked="" type="checkbox"/>
B	<input type="checkbox"/>
nced	<input type="checkbox"/>
cation	<input type="checkbox"/>
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special

A-1

The transient behavior of the optical susceptibility of polydiacetylene induced by an ultrafast pump field is investigated. Within a two-level model which includes phonon effects phenomenologically, an analytical expression for the nonlinear susceptibility is obtained. In addition to spectral hole burning, the novel phenomenon of optical nutation is found. Both this nutation and the shape of the hole depend sensitively on the detuning between the exciton frequency and the sum of the pump field and the phonon mode frequencies. The electronic state and phonon-mediated optical Stark blue shift are also found in this model. The results are in qualitative agreement with experiments and indicate that the steady-state approximation is reliable only when the pulse of the pump field is longer than several exciton lifetimes.

1988 PACS Nos.: 42.65.-k, 71.35.+z, 36.20.-r

* On leave of absence from the Shanghai Institute of Metallurgy, Chinese Academy of Sciences, Shanghai, People's Republic of China.

† Also affiliated with the Center for Electronic and Electro-optical Materials, State University of New York at Buffalo.

I. Introduction

Coherent transient interactions between materials and optical fields are one of the most interesting subjects in physics. Investigations of transient optical effects have become very important in the development of coherent optical spectroscopy and fast response nonlinear optical materials. Such studies cover such a wide spectrum of subjects and materials as photon echo, free induction decay and optical nutation in gaseous materials,¹⁻⁵ ultrafast dynamical blue shift of the exciton resonance accompanied by strong bleaching in quantum wells in heterostructure semiconductors,⁶⁻⁹ nonlinear optical response of excitons^{10,11} and large susceptibilities^{12,13} in polymers, optical nutation in direct-gap bulk semiconductors,^{14,15} and so forth.

A nonlinear optical material can be defined as one whose optical properties change when light shines upon it. In recent years, the study of coherent nonlinear optical processes produced by the excitation of semiconductors in the transparent region well below the absorption edge⁶⁻⁹ has been extended to polymers.^{10,11} When the frequency of the laser beam falling on semiconductors is tuned below the exciton resonance, it is known that virtual excitons are generated. These excitons interact with photons in exactly the same way as real excitons.^{7,9-11} Such excitonic effects can be explored more naturally by probing the susceptibility⁹ and looking for transient changes that persist as long as the excitation. The imaginary part of the susceptibility is usually examined via the absorption spectrum, and its real part is explored by measuring the index of refraction, provided that the sample is strongly excited well below the conduction band edge.

It is well known that polymers exhibit large nonlinear optical susceptibilities. In comparison with other materials, polymers have the added advantage of having extremely fast ground-state recovery times, which is why

they attract much attention for their potential applications in future generations of signal processing devices. Polydiacetylene (PDA) may be a good candidate for such considerations because of its large $\chi^{(3)}$ and small transmission loss α which can be reduced to as low as¹⁶ $\alpha < 1 \text{ db/cm}$. Thus the material possesses a fairly large ratio $\chi^{(3)}/\alpha$, which is usually the measure of the usefulness of a material employed in switching devices. Besides, PDA is easier to use in the construction of waveguides.¹⁷ In spite of the considerable amount of research carried out so far, however, the mechanism that governs its nonlinear optical response is still not well understood, although tremendous progress has made it ripe for further examination.

In this paper, we study the transient behavior of the induced optical susceptibility of polymers due to irradiation by an ultrashort pulse of a pump laser field. We take, as an example, polydiacetylene-toluene sulfonate (PTS) which is irradiated by a strong pump laser and a weak probing laser. The two lasers may have pulse duration of femtoseconds to picoseconds. For the PTS system we adopt the two-level model^{4,6,15} to describe its ground-state and virtual exciton state. The lifetime of the exciton and the mediating effects of the phonon are introduced phenomenologically. We use the perturbation technique to find the differential nonlinear susceptibility by solving analytically to all orders in the pump field and to first order in the test field.

II. Two-level model

The two electronic states of PTS are denoted by $|+\rangle$ and $|-\rangle$. We assume a dipole transition and define the dipole operators

$$\mathbf{S}^z = |-\rangle\langle+| \quad (1a)$$

$$S^+ = |+\rangle\langle -| \quad , \quad (1b)$$

with the inversion operator given by

$$S^z = \frac{1}{2} (|+\rangle\langle +| - |-\rangle\langle -|) \quad . \quad (1c)$$

For a single virtual exciton and a single phonon mode, we can write the free Hamiltonian as

$$H_0 = \hbar\omega_x S^z + \hbar\omega_i b_i^\dagger b_i \quad , \quad (2a)$$

where b_i^\dagger (b_i) creates (annihilates) a phonon in mode i with frequency ω_i , and ω_x is the exciton frequency.¹¹ For the interaction Hamiltonian we consider that each virtual exciton interacts with both a strong pump field of amplitude E_p and frequency ω_p and a weak test field of amplitude E_t and frequency ω_t . Since the test field is very weak, we assume the mediating effects of the phonons on the dipole transition to be induced only by the pump field, as shown in Fig. 1. Therefore, we can write the interaction Hamiltonian in both the rotating-wave approximation and the interaction representation as

$$H_{Pi} = -\frac{1}{2} \lambda E_p e^{i\Delta_p t} b_i^\dagger S^- + h.c. \quad (2b)$$

for the interaction between the pump field and the PTS, and

$$H_t = -\frac{1}{2} \mu E_t e^{i\Delta_t t} S^- + h.c. \quad (2c)$$

for the interaction between the test field and the PTS, where $\Delta_{p_i} = \omega_p + \omega_i - \omega_x$, $\Delta_t = \omega_t - \omega_x$, μ is the dipole matrix element, and λ is a coupling constant proportional to the transition dipole moment μ . Here we have neglected the momentum dependence of virtual excitons^{11,15} and the damping effect of the phonons. This Hamiltonian uses dipole or projection operators to describe the dipole transition between the ground state and the excitonic state of the material by external fields. It is different from that of Ref. 11, where creation and annihilation operators were used for virtual excitons.

For simplicity, we assume that each phonon mode has only two states, $|1\rangle$ and $|0\rangle$, and that the two and higher-phonon effects are negligible. The initial condition we consider here is that the system electronically is in its ground state with no virtual exciton present, while the phonon mode is in its excited state $|1\rangle$. We define $C_{i\pm}(t)$ as the probability amplitude of the state $|i\pm\rangle$ when there is the i -th phonon mode only, of which the time derivative $\dot{C}_{i\pm}$ is composed of three parts: pump field-induced part $\dot{C}_{i\pm}^p$, test field-induced part $\dot{C}_{i\pm}^t$, and damping part $\dot{C}_{i\pm}^d$. By using the Schrödinger equation and the interaction Hamiltonians (2), we obtain^{14,15}

$$\dot{C}_{i+}^{p,t}(t) = i\Omega_{p,t}^* e^{-i\Delta_{p_i,t}} C_{i-}, \quad (3a)$$

$$\dot{C}_{i-}^{p,t}(t) = i\Omega_{p,t} e^{i\Delta_{p_i,t}} C_{i+}, \quad (3b)$$

where in deriving the equation for \dot{C}_{\pm}^t we have neglected the phonon effects and have defined $\Omega_p = \lambda E_p / 2\hbar$ and $\Omega_t = \mu E_t / 2\hbar$. Then we may write the damping part phenomenologically^{14,15} as

$$\dot{C}_{i+}^d(t) = -\gamma C_{i+} \quad (4a)$$

$$\dot{C}_{i-}^d(t) = 0 \quad , \quad (4b)$$

where γ is the damping rate describing the short lifetime of the virtual exciton. Therefore, from $\dot{C}_{i\pm} = \dot{C}_{i\pm}^p + \dot{C}_{i\pm}^t + \dot{C}_{i\pm}^d$ we have the following equations for $C_{i\pm}$:

$$\dot{C}_{i+}(t) = i\Omega_p^* e^{-i\Delta_{p_i} t} C_{i-} + i\Omega_t^* e^{-i\Delta_t t} C_{i-} - \gamma C_{i+} \quad (5a)$$

$$\dot{C}_{i-}(t) = i\Omega_p^* e^{i\Delta_{p_i} t} C_{i+} + i\Omega_t^* e^{i\Delta_t t} C_{i+} . \quad (5b)$$

Since the test field is in most cases much weaker than the pump field, we can safely apply perturbation theory to solve (5). The zeroth-order equations are obtained by setting $E_t = 0$ in (5), namely,

$$\dot{C}_{i+}^0 = i\Omega_p^* e^{-i\Delta_{p_i} t} C_{i-}^0 - \gamma C_{i+}^0 \quad (6a)$$

$$\dot{C}_{i-}^0 = i\Omega_p^* e^{i\Delta_{p_i} t} C_{i+}^0 . \quad (6b)$$

In what follows, we assume for simplicity $\mu = \mu^*$, $\lambda = \lambda^*$ and $\Omega_{p,t} = \Omega_{p,t}^*$. With the initial conditions $C_{i+}^0(0) = 0$ and $C_{i-}^0(0) = 1$, we find the solutions

$$C_{i+}^0 = \frac{i\Omega_p}{\Omega_i} \sin \Omega_i t \exp[-(i\Delta_{p_i} + \gamma)t/2] \quad (7a)$$

$$c_{i\pm}^0 = (\cos \Omega_i t + \frac{\gamma - i\Delta_{p_i}}{2\Omega_i} \sin \Omega_i t) e^{(i\Delta_{p_i} - \gamma)t/2}, \quad (7b)$$

where we have defined the complex Rabi frequency

$$\Omega_i = \frac{1}{2} [(\Delta_{p_i} + i\gamma)^2 + 4\Omega_p^2]^{\frac{1}{2}}. \quad (8)$$

The real part of the Rabi frequency is given by

$$\Omega_R = [(\sqrt{x^2 + y^2} + x)/8]^{\frac{1}{2}}, \quad (9a)$$

which determines the oscillation frequency, and the imaginary part by

$$\Omega_I = -[(\sqrt{x^2 + y^2} - x)/8]^{\frac{1}{2}}, \quad (9b)$$

which determines the envelope of the oscillation. In (9) we have defined $x = \Delta_{p_i}^2 + 4\Omega_p^2 - \gamma^2$ and $y = 2\Delta_{p_i}\gamma$, with $\Delta_{p_i} < 0$.

The solutions up to first-order perturbation can be obtained by inserting the zeroth-order solutions (7) into the right-hand side of (5). The results are

$$c_{i\pm}(t) = c_{i\pm}^0(t) + \delta c_{i\pm}(t) + A_{i\pm} \quad (10)$$

$$\delta c_{i\pm} = \frac{\Omega_t \Omega_p}{\Omega_i} \frac{\exp[i\Delta_t t - \frac{1}{2}(i\Delta_{p_i} + \gamma)t]}{[\frac{1}{2}(i\Delta_{p_i} + \gamma) - i\Delta_t]^2 + \Omega_i^2}$$

$$\times \left[\left(\frac{1}{2}(i\Delta_{p_i} + \gamma) - i\Delta_t \right) \sin\Omega_i t + \Omega_i \cos\Omega_i t \right] \quad (11a)$$

$$\begin{aligned} \delta C_{i+} &= \frac{i\Omega_t}{2\Omega_i} \frac{\exp[-i\Delta_t t + \frac{1}{2}(i\Delta_{p_i} - \gamma)t]}{\left[i\Delta_t - \frac{1}{2}(i\Delta_{p_i} - \gamma) \right]^2 + \Omega_i^2} \\ &\times \left[(\Delta_{p_i} + i\gamma)^2 + 2\Omega_p^2 + i\Delta_t(i\Delta_{p_i} - \gamma) \right] \sin\Omega_i t \\ &- 2\Omega_i [i(\Delta_t - \Delta_{p_i}) + \gamma] \cos\Omega_i t \end{aligned} \quad (11b)$$

The integration constants $A_{i\pm}$ in (10) are determined by the initial conditions.

The expectation value of the dipole moment of a virtual exciton is

$$\begin{aligned} \mu_i(t) &= \mu \langle S^-(t) \rangle_i e^{-i\omega_x t} = \mu C_{i-}^* C_{i+} e^{-i\omega_x t} \\ &= \mu (C_{i-}^{0*} + \delta C_{i-}^* + A_{i-}^*) (C_{i+}^0 + \delta C_{i+} + A_{i+}) e^{-i\omega_x t} \end{aligned} \quad (12)$$

It is evident that the dipole moment induced by the test beam is given by

$$\delta\mu_i(t) = \mu (C_{i-}^0 * \delta C_{i+} + C_{i+}^0 \delta C_{i-}^*) e^{-i\omega_x t} \quad (13)$$

Therefore, the nonlinear optical susceptibility experienced by the test beam is simply

$$\begin{aligned}
x_i &= n_i \delta \mu_i(t) / (E_t e^{-i\omega_t t}) \\
&= i n_i \frac{|\mu|^2}{2\hbar} e^{-\gamma t} \left(\frac{1}{2\Omega_i z_1^i} [\cos\Omega_i^* t + i \frac{\Delta_{p_i} - i\gamma}{2\Omega_i^*} \sin\Omega_i^* t] \right. \\
&\quad \times [((\Delta_{p_i} + i\gamma)^2 + 2\Omega_p^2 - \Delta_t(\Delta_{p_i} + i\gamma)) \sin\Omega_i t \\
&\quad \left. - 2\Omega_i(i(\Delta_t - \Delta_{p_i}) + \gamma) \cos\Omega_i t] \right. \\
&\quad \left. - \frac{\Omega_p^2}{|\Omega_i|^2 z_2^i} \sin\Omega_i t [(\frac{1}{2}(i\Delta_{p_i} - \gamma) - i\Delta_t) \sin\Omega_i^* t + \Omega_i^* \cos\Omega_i^* t] \right) , \quad (14)
\end{aligned}$$

where

$$z_1^i = [\frac{1}{2}(i\Delta_{p_i} - \gamma) - i\Delta_t]^2 + \Omega_i^2 \quad (15a)$$

$$z_2^i = [\frac{1}{2}(i\Delta_{p_i} - \gamma) + i\Delta_t]^2 + \Omega_i^2 . \quad (15b)$$

We have introduced in (14) the optically-induced transient virtual exciton density n_i which is taken to be proportional to the probability of virtual exciton state,¹⁸

$$n_i = n_s C_{i+}^0 C_{i+}^{0*} = n_s \frac{\Omega_p^2}{|\Omega_i|^2} |\sin\Omega_i t|^2 \exp(-\gamma t) , \quad (16)$$

where we have assumed that all the virtual excitons are induced by the pump field E_p , since those induced by the weaker probe field are much less likely, and n_s is the saturation density of the virtual excitons. In this paper we only consider the two phonon modes coupling most strongly to the exciton,¹⁹ so that we have the nonlinear susceptibility

$$x_t = \sum_{i=1}^2 x_i . \quad (17)$$

The transient behavior of the nonlinear optical susceptibility x_t is calculated numerically as a function of time and the frequencies ω_p and ω_t . The results are presented and discussed in the next section.

III. Results and discussion

In our numerical study, we have used the unit $\hbar = 1$. Other parameters are chosen as^{10,11,20} $\omega_1 = 0.184$ eV, $\omega_2 = 0.258$ eV, $\gamma = 0.02$ eV, $\frac{1}{e}|\mu|^2 n_s = \frac{1}{40\pi}$ eV, $\Omega_p = 5 \times 10^{-4}$ eV and $\omega_x = 1.978$ eV. The real and imaginary parts of x_t are computed separately. Figure 2 shows snapshots at different instants of time of the variation of x_t with the pump detuning. The variation with time for fixed detuning is shown in Fig. 3. Figure 4 shows snapshots at different instants of time of the imaginary part of x_t when the resonance condition is satisfied, i.e., $\omega_x = \omega_p + \omega_2$.

It is clearly seen from Fig. 2 that both the differential absorption and refraction are direct effects of the virtual excitons induced by the pump field. The mediating role played by the phonon is substantial when the duration of the pump pulse is long enough (see the two peaks of the imaginary part, where $\omega_x = \omega_p + \omega_i$). This is in agreement with the experimental results

of Ref. 11. However, when the duration of the pump pulse is short, e.g., less than the lifetime of the virtual exciton, the peak structure of the imaginary part is not clear, i.e., we cannot see evident optical phonon-mediated effects. It should be noted at this point that the present results are different from those reported in Ref. 21 in which steady-state susceptibilities are calculated in the three-level two-field model without phonon effects.

Optical nutation can be observed in polymers in the ultrashort time regime when virtual excitons are generated by a pump field tuned below the exciton resonance. This situation can be seen from Fig. 3. However, when the sum of the pump field frequency and one of the phonon frequencies is on resonance with the exciton frequency, the Rabi oscillation amplitude becomes smaller. This reflects the fact that the optical phonon plays a crucial role in the optical nutation of PTS. It is also clearly shown that sometimes the oscillation centers of $\text{Im}x_t$ change with time. This is quite different from nutation phenomena predicted in Refs. 14 and 15 for semiconductors where the oscillation amplitude decreases monotonically like damped oscillators.

From Fig. 4, we can see the transient behavior of the spectral hole burning, which also needs sufficient long duration of the pump pulse to have an effect. The hole is close to the exciton resonance, and there is a deeper hole when $\omega_x = \omega_p + \omega_i$. This indicates that there is energy transfer from the pump field to the test field via optical phonons and virtual excitons, also in qualitative agreement with experiments.^{10,11}

Since it takes time for the pump field to build up enough virtual excitons and since the virtual excitons are short-lived, their effects are appreciable and stable most of the time during the pulse (on the order of picoseconds). The response time can be anywhere between 20 - 200 femtoseconds

according to our calculation. Both the absorption and refraction parts show up almost right away and taper off rather slowly after reaching their peaks. So, for longer excitation time of the pump field, say, several times of the exciton lifetime, the steady-state method may be reliable.

In addition, we have also found that increasing the intensity of the pump field leads to a deeper and wider hole in the absorption spectrum, which is qualitatively in agreement with the steady-state results of Ref. 11. What seems to be more interesting is that we find a blue shift of 0.005 eV in our calculation. This represents joint effects of both the phonon-induced optical Stark shift and the electronic state optical Stark shift. Such effects have been observed in a recent experiment²⁰ in which the differential transmission of polydiacetylene-toluene sulfonate has been measured by means of coherent inverse Raman spectroscopy. It is demonstrated in Ref. 20 that this ac Stark effect is important in the determination of the nonlinear optical response of PTS even in the small signal limit. The effect is reproduced theoretically in Ref. 20 by including an extra term to modify the exciton resonance frequency in the simple model of Schmitt-Rink et al.¹¹ However, we need not do so, and the treatment in both Refs. 11 and 20 assumes a steady-state solution while the experimental conditions are more transient-like.

Acknowledgments

This research was supported by the Air Force Office of Scientific Research (AFSC), United States Air Force, under Contract F49620-86-C-0009, and the Office of Naval Research. The United States Government is authorized to copy and distribute reprints for governmental purposes notwithstanding any copyright notation hereon.

References

1. R. G. Brewer and R. L. Shoemaker, Phys. Rev. Lett. 27, 631 (1971).
2. S. L. McCall and E. L. Hahn, Phys. Rev. A 2, 861 (1970).
3. R. G. Brewer, in Nonlinear Optics, ed. by P. G. Harper and B. S. Wherett (Academic, London, 1977), p. 307 ff.
4. L. Allen and J. H. Eberly, Optical Resonance and Two-level Atoms (Wiley, New York, 1975).
5. Y. R. Shen, The Principles of Nonlinear Optics (Wiley, New York, 1984).
6. A. Mysyrowicz, D. Hulin, A. Antonetti, A. Migns, W. T. Masselink and H. Morkoc, Phys. Rev. Lett. 56, 2748 (1986).
7. S. Schmitt-Rink and D. S. Chemla, Phys. Rev. Lett. 57, 2752 (1986).
8. A. Von Lenman, D. S. Chemla, J. E. Zucker and J. P. Heritage, Opt. Lett. 11, 609 (1986).
9. D. S. Chemla, D. A. B. Miller and S. Schmitt-Rink, in Optical Nonlinearities and Instabilities in Semiconductors, ed. by H. Haug (Academic, New York, 1988), p. 83 ff.
10. B. I. Greene, J. Orenstein, R. R. Millard and L. R. Williams, Chem. Phys. Lett. 139, 381 (1987); Phys. Rev. Lett. 58, 2750 (1987).
11. B. I. Green, J. F. Mueller, J. Orenstein, D. H. Rapkine, S. Schmitt-Rink and M. Thakur, Phys. Rev. Lett. 61, 325 (1988).
12. See, for example, Nonlinear Optical Properties of Organic Molecules and Crystals, ed. by D. S. Chemla and J. Zyss (Academic, New York, 1987).
13. G. M. Carter, Y. J. Chen and S. K. Tripathy, Appl. Phys. Lett. 43, 891 (1983).
14. P. Sen and P. K. Sen, IEEE J. Quantum Electron. QE23, 2033 (1987).
15. K. Singh, P. Sen and P. K. Sen, IEEE J. Quantum Electron. QE25, 67 (1989).

16. P. D. Townsend, G. L. Baker, N. E. Schlotter and S. Etemad, *Synth. Met.* 28, D633 (1989).
17. M. Thakur, Y. Shani, G. C. Chi and K. O'Brian, *Synth. Met.* 28, D595 (1989).
18. C. H. B. Cruz, J. P. Gordon, P. C. Becker, R. L. Fork and C. V. Shank, *IEEE J. Quantum Electron.* QE24, 261 (1988).
19. See D. N. Batchelder in Polydiacetylenes, ed. by D. Bloor and R. R. Chance (Martinus Nijhoff, Dordrecht, The Netherlands, 1985), p. 187 ff.
20. G. J. Blanchard, J. P. Heritage, A. C. Von Lehmen, G. L. Baker and S. Etemad, *Bull. Am. Phys. Soc.* 34, 452 (1989).
21. S. Saikan, N. Hashimoto, T. Kushida and K. Namba, *J. Chem. Phys.* 82, 5409 (1985).

Figure captions

1. Two-level model representing the excitonic state $|+\rangle$ and ground state $|-\rangle$.
The virtual excitons are induced by a strong pump field with frequency ω_p .
Each transitions is mediated by a single phonon of frequency ω_i , such that
 $\omega_p + \omega_i = \omega_x$ on resonance.
2. Snapshots of the real (curve 1) and imaginary (curve 2) parts of the nonlinear susceptibility versus pump detuning at various times for $\omega_t = \omega_x$: (a) $t = 25 \text{ (eV)}^{-1}$, (b) $t = 100 \text{ (eV)}^{-1}$, (c) $t = 500 \text{ (eV)}^{-1}$, (d) $t = 3500 \text{ (eV)}^{-1}$.
3. Real (curve 1) and imaginary (curve 2) parts of x_t versus time for $\omega_t = \omega_x$: (a) $\omega_p = 1.6 \text{ eV}$; (b) $\omega_p = 1.72 \text{ eV}$.
4. Snapshots of the imaginary part of the susceptibility versus probe frequency when $\omega_p = 1.72 \text{ eV}$: (a) $t = 25 \text{ (eV)}^{-1}$, (b) $t = 500 \text{ (eV)}^{-1}$, (c) $t = 3500 \text{ (eV)}^{-1}$.

Fig. 1

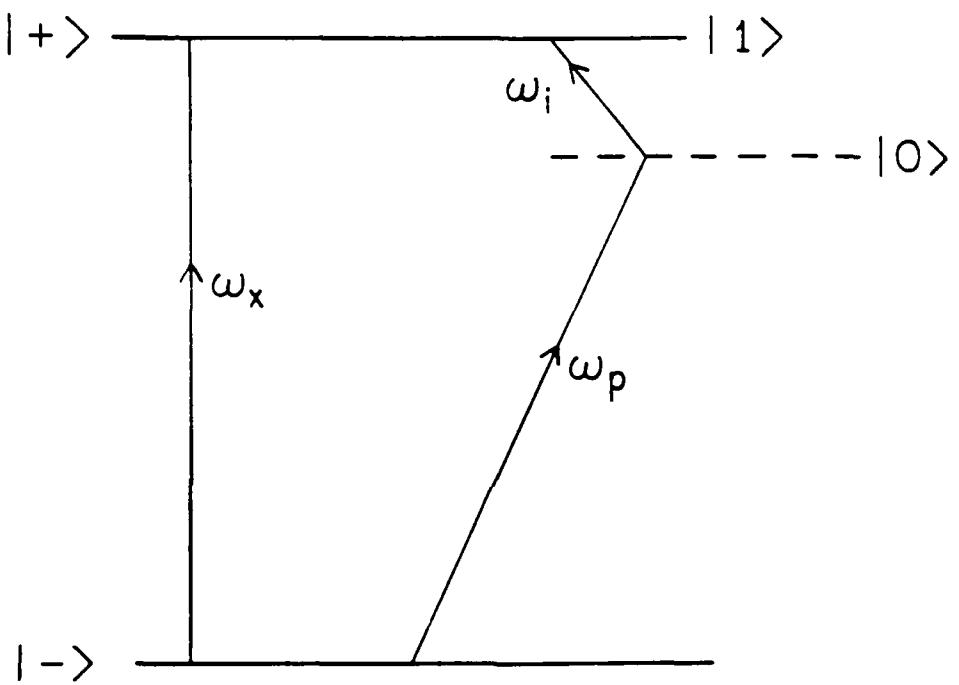


Fig. 2

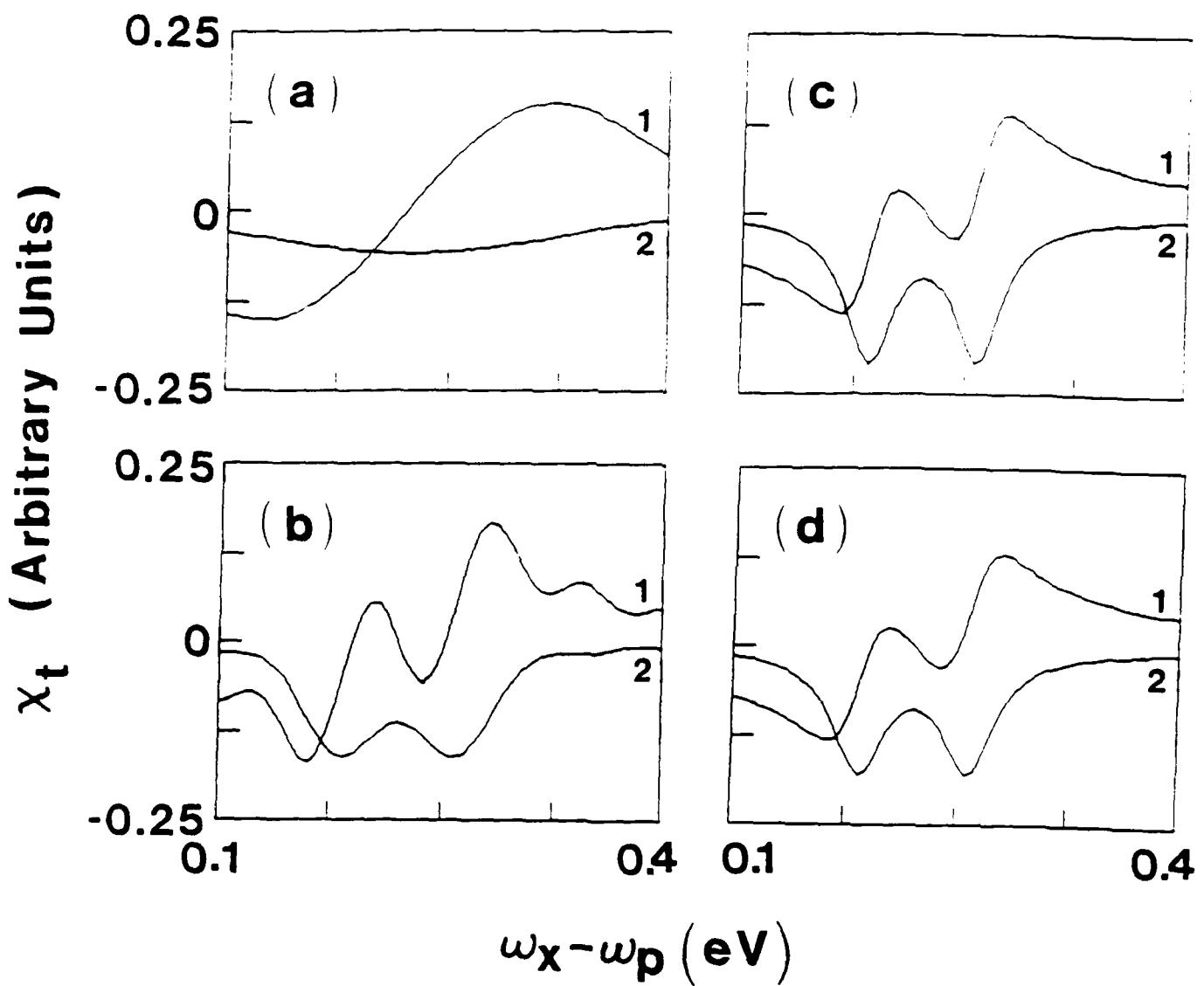


Fig. 3
c

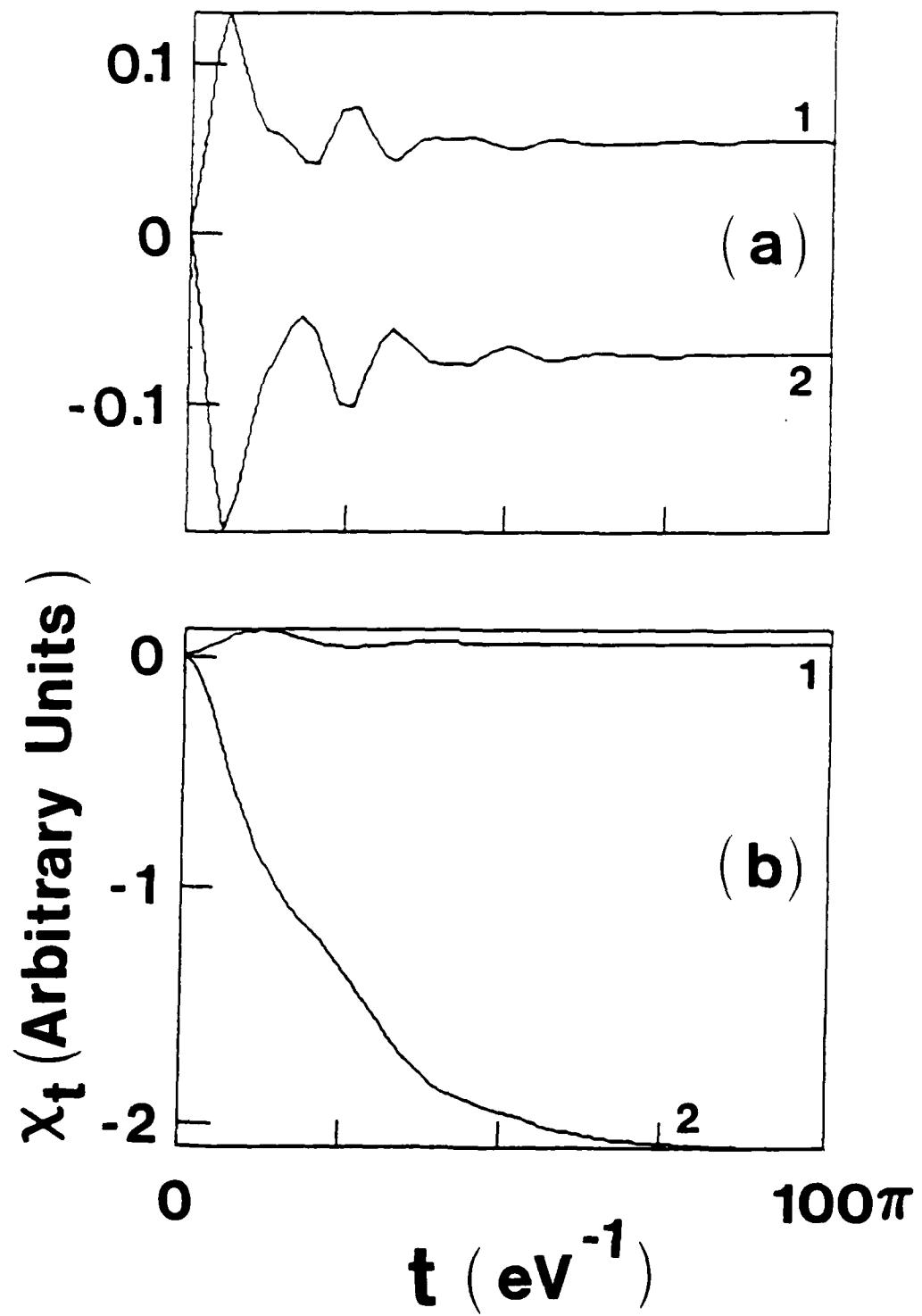
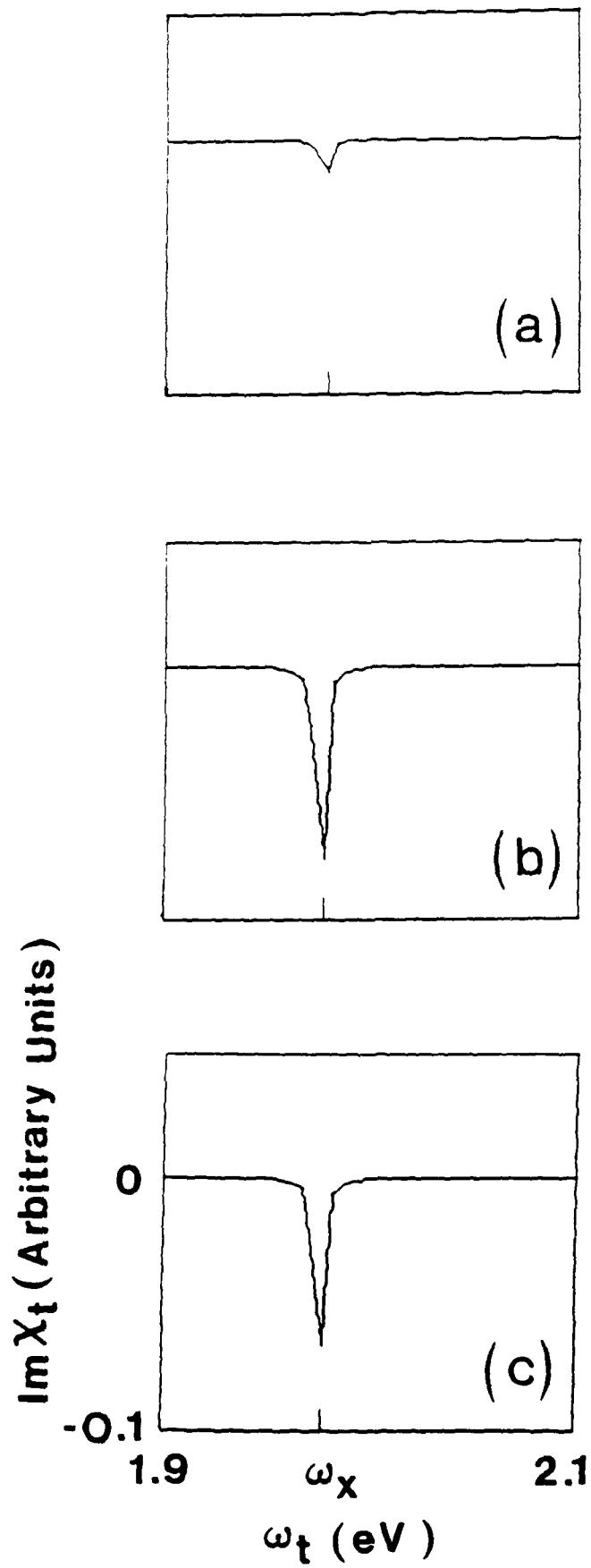


Fig. 4



DL/1113/86/2

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Attn: Code 1113 800 N. Quincy Street Arlington, Virginia 22217-5000	2	Dr. David Young Code 334 NORDA NSTL, Mississippi 39529	1
Dr. Bernard Douda Naval Weapons Support Center Code 50C Crane, Indiana 47522-5050	1	Naval Weapons Center Attn: Dr. Ron Atkins Chemistry Division China Lake, California 93555	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko, Code L52 Port Hueneme, California 93401	1	Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12 high quality	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
DTNSRDC Attn: Dr. H. Singerman Applied Chemistry Division Annapolis, Maryland 21401	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000	1	Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1
		Dr. David L. Nelson Chemistry Division Office of Naval Research 800 North Quincy Street Arlington, Virginia 22217	1

ABSTRACTS DISTRIBUTION LIST, 056/625/629

Dr. J. E. Jensen
Hughes Research Laboratory
3011 Malibu Canyon Road
Malibu, California 90265

Dr. C. B. Harris
Department of Chemistry
University of California
Berkeley, California 94720

Dr. J. H. Weaver
Department of Chemical Engineering
and Materials Science
University of Minnesota
Minneapolis, Minnesota 55455

Dr. F. Kutzler
Department of Chemistry
Box 5055
Tennessee Technological University
Cookeville, Tennessee 38501

Dr. A. Reisman
Microelectronics Center of North Carolina
Research Triangle Park, North Carolina
27709

Dr. D. DiLella
Chemistry Department
George Washington University
Washington D.C. 20052

Dr. M. Grunze
Laboratory for Surface Science and
Technology
University of Maine
Orono, Maine 04469

Dr. R. Reeves
Chemistry Department
Rensselaer Polytechnic Institute
Troy, New York 12181

Dr. J. Butler
Naval Research Laboratory
Code 6115
Washington D.C. 20375-5000

Dr. Steven M. George
Stanford University
Department of Chemistry
Stanford, CA 94305

Dr. L. Interante
Chemistry Department
Rensselaer Polytechnic Institute
Troy, New York 12181

Dr. Mark Johnson
Yale University
Department of Chemistry
New Haven, CT 06511-8118

Dr. Irvin Heard
Chemistry and Physics Department
Lincoln University
Lincoln University, Pennsylvania 19352

Dr. W. Knauer
Hughes Research Laboratory
3011 Malibu Canyon Road
Malibu, California 90265

Dr. K.J. Klaubunde
Department of Chemistry
Kansas State University
Manhattan, Kansas 66506

ABSTRACTS DISTRIBUTION LIST, 056/625/629

Dr. G. A. Somorjai
Department of Chemistry
University of California
Berkeley, California 94720

Dr. J. Murday
Naval Research Laboratory
Code 6170
Washington, D.C. 20375-5000

Dr. J. B. Hudson
Materials Division
Rensselaer Polytechnic Institute
Troy, New York 12181

Dr. Theodore E. Madey
Surface Chemistry Section
Department of Commerce
National Bureau of Standards
Washington, D.C. 20234

Dr. J. E. Demuth
IBM Corporation
Thomas J. Watson Research Center
P.O. Box 218
Yorktown Heights, New York 10598

Dr. M. G. Lagally
Department of Metallurgical
and Mining Engineering
University of Wisconsin
Madison, Wisconsin 53706

Dr. R. P. Van Duyne
Chemistry Department
Northwestern University
Evanston, Illinois 60637

Dr. J. M. White
Department of Chemistry
University of Texas
Austin, Texas 78712

Dr. D. E. Harrison
Department of Physics
Naval Postgraduate School
Monterey, California 93940

Dr. R. L. Park
Director, Center of Materials
Research
University of Maryland
College Park, Maryland 20742

Dr. W. T. Peria
Electrical Engineering Department
University of Minnesota
Minneapolis, Minnesota 55455

Dr. Keith H. Johnson
Department of Metallurgy and
Materials Science
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Dr. S. Sibener
Department of Chemistry
James Franck Institute
5640 Ellis Avenue
Chicago, Illinois 60637

Dr. Arnold Green
Quantum Surface Dynamics Branch
Code 3817
Naval Weapons Center
China Lake, California 93555

Dr. A. Wold
Department of Chemistry
Brown University
Providence, Rhode Island 02912

Dr. S. L. Bernasek
Department of Chemistry
Princeton University
Princeton, New Jersey 08544

Dr. W. Kohn
Department of Physics
University of California, San Diego
La Jolla, California 92037

DL/1113/86/2

ABSTRACTS DISTRIBUTION LIST, 056/625/629

Dr. F. Carter
Code 6170
Naval Research Laboratory
Washington, D.C. 20375-5000

Dr. Richard Colton
Code 6170
Naval Research Laboratory
Washington, D.C. 20375-5000

Dr. Dan Pierce
National Bureau of Standards
Optical Physics Division
Washington, D.C. 20234

Dr. R. Stanley Williams
Department of Chemistry
University of California
Los Angeles, California 90024

Dr. R. P. Messmer
Materials Characterization Lab.
General Electric Company
Schenectady, New York 22217

Dr. Robert Gomer
Department of Chemistry
James Franck Institute
5640 Ellis Avenue
Chicago, Illinois 60637

Dr. Ronald Lee
R301
Naval Surface Weapons Center
White Oak
Silver Spring, Maryland 20910

Dr. Paul Schoen
Code 6190
Naval Research Laboratory
Washington, D.C. 20375-5000

Dr. John T. Yates
Department of Chemistry
University of Pittsburgh
Pittsburgh, Pennsylvania 15260

Dr. Richard Greene
Code 5230
Naval Research Laboratory
Washington, D.C. 20375-5000

Dr. L. Kesmodel
Department of Physics
Indiana University
Bloomington, Indiana 47403

Dr. K. C. Janda
University of Pittsburgh
Chemistry Building
Pittsburg, PA 15260

Dr. E. A. Irene
Department of Chemistry
University of North Carolina
Chapel Hill, North Carolina 27514

Dr. Adam Heller
Bell Laboratories
Murray Hill, New Jersey 07974

Dr. Martin Fleischmann
Department of Chemistry
University of Southampton
Southampton SO9 5NH
UNITED KINGDOM

Dr. H. Tachikawa
Chemistry Department
Jackson State University
Jackson, Mississippi 39217

Dr. John W. Wilkins
Cornell University
Laboratory of Atomic and
Solid State Physics
Ithaca, New York 14853

AL/1113/86/2

ABSTRACTS DISTRIBUTION LIST, 056/625/629

Dr. R. G. Wallis
Department of Physics
University of California
Irvine, California 92664

Dr. D. Ramaker
Chemistry Department
George Washington University
Washington, D.C. 20052

Dr. J. C. Hemminger
Chemistry Department
University of California
Irvine, California 92717

Dr. T. F. George
Chemistry Department
University of Rochester
Rochester, New York 14627

Dr. G. Rubloff
IBM
Thomas J. Watson Research Center
P.O. Box 218
Yorktown Heights, New York 10598

Dr. Horia Metiu
Chemistry Department
University of California
Santa Barbara, California 93106

Dr. W. Goddard
Department of Chemistry and Chemical
Engineering
California Institute of Technology
Pasadena, California 91125

Dr. P. Hansma
Department of Physics
University of California
Santa Barbara, California 93106

Dr. J. Baldeschwieler
Department of Chemistry and
Chemical Engineering
California Institute of Technology
Pasadena, California 91125

Dr. J. T. Keiser
Department of Chemistry
University of Richmond
Richmond, Virginia 23173

Dr. R. W. Plummer
Department of Physics
University of Pennsylvania
Philadelphia, Pennsylvania 19104

Dr. E. Yeager
Department of Chemistry
Case Western Reserve University
Cleveland, Ohio 41106

Dr. N. Winograd
Department of Chemistry
Pennsylvania State University
University Park, Pennsylvania 16802

Dr. Roald Hoffmann
Department of Chemistry
Cornell University
Ithaca, New York 14853

Dr. A. Steckl
Department of Electrical and
Systems Engineering
Rensselaer Polytechnic Institute
Troy, New York 12181

Dr. G.H. Morrison
Department of Chemistry
Cornell University
Ithaca, New York 14853